the data of Reid and Mulliken[14] to 57° yields an equilibrium constant for complex formation of 80 l. mole^{-1}. Since the $RO_2\cdot$ radical is believed to have an electron affinity of 70 kcal. mole^{-1},[15] while this value for iodine is 54.6 kcal. mole^{-1},[16] it is surprising that the cumylperoxy radical–pyridine complex appears weak. Other factors, however, influence complex stability.

The choice of pyridine as a representative donor may be criticized for the present purpose of evaluating the extent of complex formation between cumylperoxy radicals and oxidation inhibitors. Unfortunately, the aromatic amine oxidation inhibitors themselves cannot be used in these types of studies because they both lower the steady state $RO_2\cdot$ concentration and give rise to relatively high concentrations of disubstituted nitric oxide radicals.[8] E.s.r. studies with triphenylamine, similar to those described above for pyridine, have been conducted with the result that K can be said to be less than 4 l. mole^{-1} at 57°. Studies with N,N-dimethylaniline and diphenylmethylamine have not yielded interpretable results because of complications which they produce upon the oxidation rate when used at high concentrations.

With iodine the ΔH values for complexes with pyridine (-7.8 kcal. mole^{-1}), N,N-dimethylaniline (-8.2 kcal. mole^{-1}) and trimethylamine (-12.0 kcal. mole^{-1})

(14) C. Reid and R. S. Mulliken, J. Am. Chem. Soc., 76, 3869 (1954).
(15) H. O. Pritchard, Chem. Revs., 52, 529 (1953).
(16) R. S. Mulliken, J. Am. Chem. Soc., 72, 600 (1950).

parallel basicity, pK values of 5.19, 5.21, and 10.7, respectively,[17] while formation constants at 57° are 80, 6.3, and 1700 l. mole^{-1}, respectively. Less basic diphenylamine, pK = 0.85, would be expected to be a poorer n-donor than pyridine; and it seems doubtful that its formation constant for complexing with cumylperoxy radical would be significantly larger than that of pyridine.

With regard to the charge-transfer complex mechanism of oxidation inhibition, these results indicate that the termination reaction 9 must be very rapid. For diphenylamine the product Kk_9 has been shown[8] to

$$RO_2\cdot + [RO_2\cdot \ldots I_n] \rightarrow X \, k_9 \qquad (9)$$
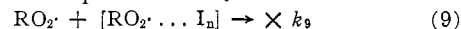
have a value of 3.6×10^9 l.^{2} mole^{-2} sec.$^{-1}$. With K small, k_9 must be close to the diffusion limited value. The possibility remains, of course, that the charge-transfer complex mechanism is incorrect and the kinetic observations which support it should be explained by an alternate mechanism. To date, however, no plausible alternate has been suggested.

NOTE ADDED IN PROOF.—For discussion of the nil complex formation between oxygen and pyridine see H. Tsubomura and R. S. Mulliken, J. Am. Chem. Soc., 82, 5969 (1960).

Acknowledgment.—The author is indebted to Dr. J. C. Baird for assistance with the e.s.r. measurements and to Professor P. D. Bartlett for helpful discussion concerning the status of the termination reaction of cumylperoxy radicals.

(17) H. Tsubomura, ibid., 82, 40 (1960).

Oxidation Inhibition by Trialkylamines

BY J. R. THOMAS

Trialkylamines at low concentrations inhibit the oxidation of cumene in accordance with the Boozer–Hammond mechanism. At higher concentrations, however, the inhibited rates become independent of amine concentration. This behavior is taken as evidence that cumylperoxy radical–trialkylamine complexes undergo chain propagation and self-termination reactions in addition to the simple Boozer–Hammond reactions of strong inhibitors such as diphenylamine. Electron spin resonance studies indicate that the equilibrium constants for complex formation of cumylperoxy radical with triethylamine and tri-n-butylamine are less than 53 and 86 l. mole^{-1}, respectively.

Trialkylamines are recognized inhibitors of high temperature gas-phase hydrocarbon oxidation.[1,2] However, to our knowledge, their study as liquid-phase inhibitors has not been reported. Their behavior is of particular interest in view of their great tendency to act as donors in charge-transfer complex formation. The Boozer–Hammond[3] mechanism of oxidation inhibition postulates such complex formation in a critical step as formulated. This paper describes studies of triethyl- and tri-n-butylamines as inhibitors for the oxidation of

$$RO_2^0 + I_n \rightleftharpoons [RO_2^- \ldots I_n^+]$$
$$[RO_2^- \ldots I_n^+] + RO_2\cdot \longrightarrow x$$
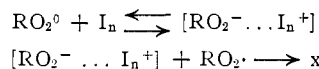
cumene and interprets the results in terms of charge-transfer complexes of these materials with cumylperoxy radical.

Experimental

The apparatus and techniques for oxidation rate and electron spin resonance (e.s.r.) measurements have been described.[4,5] Cumene was Eastman white label material passed through a silica column. Azobisisobutyronitrile was recrystallized from methanol.

(1) G. Dixon-Lewis and J. W. Linnett, Proc. Roy. Soc. (London), A210, 48 (1951).
(2) D. J. Waddington, ibid., A265, 436 (1962).
(3) C. E. Boozer and G. S. Hammond, J. Am. Chem. Soc., 76, 3861 (1954).
(4) J. R. Thomas and C. A. Tolman, ibid., 84, 2930 (1962).
(5) J. R. Thomas, ibid., 85, 591 (1963).

Triethyl- and tri-n-butylamines were Eastman white label chemicals purified by distillation.

Results and Discussion

Trialkylamines are reasonably active inhibitors for the oxidation of cumene at 70°. Initial inhibited oxidation rates, initiated by azobisisobutyronitrile (AIBN), are proportional to [AIBN]$^{1/2}$ as required by the Boozer–Hammond mechanism. The dependence upon trialkylamine concentration is surprising, however, as shown by the data plotted in Fig. 1, where initial rates are plotted against the inverse square root of the inhibitor concentration. In all cases, the substrate was 4 M cumene in chlorobenzene with 4×10^{-3} M AIBN as initiator.

The surprising feature of the data is the fact that at high concentrations the rate becomes essentially independent of amine concentration. This behavior is not due to a reduction of the kinetic chain length to near one as can be demonstrated by the fact that diphenylamine at modest concentration (10^{-3} M) reduces the rate by more than an additional order of magnitude.

The only mechanism, apparent to us, to explain the observed behavior is an extension of the charge-transfer complex postulate. This mechanism, which is outlined below, contains the normal Boozer–Hammond sequence, (3) and (4), but also allows for chain propagation by the complex species (5) and bimolecular com-
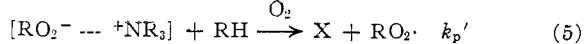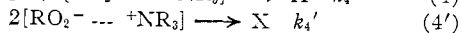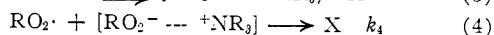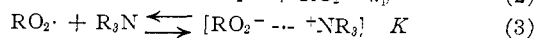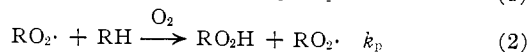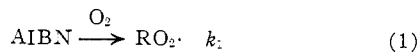
$$AIBN \xrightarrow{O_2} RO_2 \cdot \quad k_i \tag{1}$$

$$RO_2 \cdot + RH \xrightarrow{O_2} RO_2H + RO_2 \cdot \quad k_p \tag{2}$$

$$RO_2 \cdot + R_3N \xrightleftharpoons{} [RO_2^- --- {}^+NR_3] \quad K \tag{3}$$

$$RO_2 \cdot + [RO_2^- --- {}^+NR_3] \longrightarrow X \quad k_4 \tag{4}$$

$$2[RO_2^- --- {}^+NR_3] \longrightarrow X \quad k_4' \tag{4'}$$

$$[RO_2^- --- {}^+NR_3] + RH \xrightarrow{O_2} X + RO_2 \cdot \quad k_p' \tag{5}$$

plex chain termination (4'). This yields the steady-state kinetic expression (6) for the initial inhibited rate, R_i

$$R_i = [RH](k_i[AIBN])^{1/2} \left\{ \frac{k_p + Kk_p'[I_n]}{(2Kk_4[I_n] + 2K^2k_4'[I_n]^2)^{1/2}} \right\} \tag{6}$$

With $k_i = 2.8 \times 10^{-5}$ sec.$^{-1}$ and $k_p = 0.66$ l./mole sec. the solid curve in Fig. 1 was calculated by (6) using $Kk_p' = 574$ l.^{2} mole^{-2} sec.$^{-1}$, $Kk_4 = 3.6 \times 10^6$ l.^{2} mole^{-2} sec.$^{-1}$ and $K^2k_4' = 5.1 \times 10^{11}$ l.^{3} mole^{-3} sec.$^{-1}$ for triethylamine. For tributylamine the parameters are 1.14×10^3, 3.5×10^5 and 8.5×10^{11}, respectively. These values were determined by a line fitting procedure employing a digital computer.
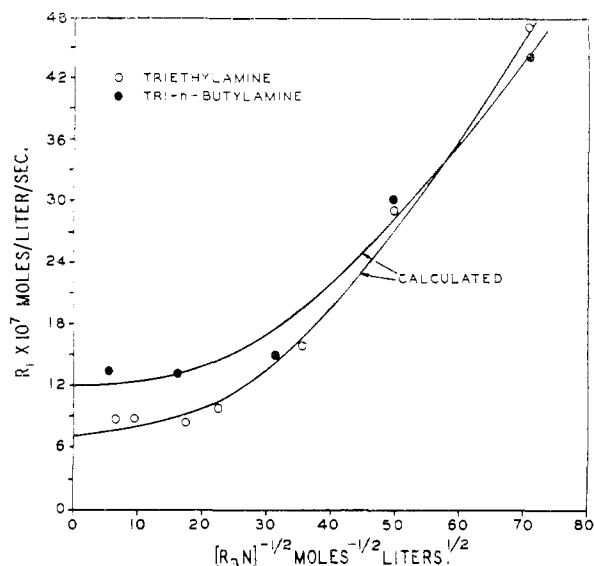

Fig. 1.—Inhibited oxidation rate as a function of trialkylamine concentration: 4 M cumene, 4 × 10^{-3} M AIBN, 70.0°.

The excellent agreement between observed and calculated values offers support for the mechanism outlined above. It is interesting to compare the value of $Kk_4 = 1.3 \times 10^9$ l.^{2} mole^{-2} sec.$^{-1}$ for diphenylamine under identical conditions[4] with those for trialkylamines. The much higher value for diphenylamines, which follows the simple Boozer and Hammond kinetics, could prevent observation of analogous reactions 4' and 5 of the complex species in this case.

In the preceding article,[5] the quantitative determination of cumylperoxy radical in oxidizing cumene by electron spin resonance is described. With the same technique solutions inhibited by triethylamine and tributylamine at 0.03 M, which is well into the limiting high concentration range, were examined. Under these conditions, no resonance absorption was detectable. The limit of detectability of the $RO_2 \cdot$ radical was about $^1/_{20}$ of its uninhibited value, and the limiting oxidation rates are reduced only $^1/_6$ for tributylamine and $^1/_{10}$ for triethylamine from the uninhibited rates. This indicates that the chain is not being propagated by the $RO_2 \cdot$ radical but by a second species, namely, the complex, in accordance with the above discussion. Assuming that the e.s.r. line width of the complex is narrow enough to be detected it can be said that K is less than 53 l./mole for triethylamine and 86 l./mole for tributylamine. The previous article sets K for pyridine at 1 or less. It is interesting to note that K for the iodine–triethylamine complex is 880 l./mole at 70° from the data of Nagakura.[6]

The peculiar behavior of trialkylamines as oxidation inhibitors affords additional evidence in favor of the charge-transfer complex mechanism of Boozer and Hammond for oxidation inhibition. It seems clear that the equilibrium constant for formation of complex species between $RO_2 \cdot$ radicals and amine-type inhibitors is small. The resulting complexes must, however, engage in very rapid chain termination reactions with $RO_2 \cdot$ radicals when an abstractable hydrogen is available as in diphenylamine. A similar, although slower, reaction appears to take place when less available hydrogen is present as in the n-alkylamines. It is also interesting to note that k_p' the propagation rate constant via complex, must be greater than 11 and 13 l. mole^{-1} sec.$^{-1}$ for triethyl- and tributylamines, respectively, considerably larger than that for uncomplexed radical. Complexed radical might be expected to react more slowly and more selectively in the manner of chlorine atoms as observed by Russell.[7]

(6) S. Nagakura, J. Am. Chem. Soc., **80**, 520 (1958).

(7) G. A. Russell, ibid., **80**, 4987 (1958).

Folded Conformations and Optically Active Triarylarsines[1]

BY KURT MISLOW, ABRAHAM ZIMMERMAN AND JOSEPH T. MELILLO

Homo- and heterocyclic 9,10-dihydroanthracenes (I) exist in folded or "butterfly" conformations. The question of conformational stability is discussed, and it is argued that the reported stereoisomerism in phenoxarsines and in 5,10-dihydroarsanthrenes is best ascribed to the optical stability of the arsenic pyramid. The preparation of an optically active acyclic triarylarsine (VI) and of an optically active 5,10-dihydroarsacridine (IX) lends strong support to these arguments.

It has been pointed out[2] that molecules of type I (XCC = YCC = 120°) cannot be coplanar unless CXC = CYC = 120°. Such molecules are folded about the

(2) E.g., I. G. M. Campbell, C. G. Le Fèvre, R. J. W. Le Fèvre and E. E. Turner, J. Chem. Soc., 404 (1938); N. J. Leonard and L. E. Sutton, J. Am. Chem. Soc., **70**, 1564 (1948), and references cited therein.
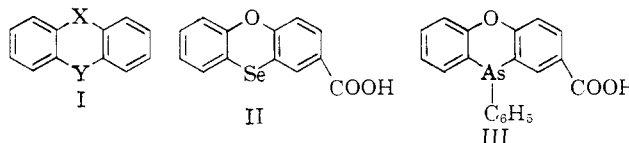
XY-axis and give rise to folded conformations (butterfly conformations).